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Conformational mobility of small molecules in glass-forming solutions studied by FTIR spectroscopy

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ABSTRACT

Small molecules with two or more stable conformations when embedded in a glass-forming liquid (matrix) serve the role of "conformational probes", *i.e.*, their conformational transitions are used to follow local mobility in the matrix. In the present study, conformational probes were embedded in low-molecular-weight glass-forming liquids, and the molecular mobility was studied in a broad temperature range including the glass transition temperature (T_g). Paraffin oil, dibutylphthalate, bis(2-ethylhexyl)phthalate and isopropylbenzene were used as glass-forming liquids while 1,2-dichloroethane, 1,2-diphenylethane, chlorocyclohexane and bromocyclohexane were used as conformational probes. For some of the matrix/probe systems, the conformational mobility was found to freeze-in at T_g, while for the others it froze-in at certain temperatures $T_f < T_g$. In the latter case, it was possible to evaluate the activation energies related to mobility of free volume entities in the glassy matrices. In addition, it was possible to estimate the volumes of sub-molecular groups of the matrix that freeze-in at T_f.

1. Introduction

Physical and chemical properties of amorphous solids are strongly affected by the glass formation conditions and local molecular mobility in the glassy state. The molecular mobility of low- and high-molecular-weight glass forming liquids has been extensively studied by different physical methods, including those based on molecular probes (see [1] and references therein). In particular, it was proposed to use compounds with conformational flexibility as probes in glassy solids [2,3]. Any molecule having two or more stable conformations detectable by infrared spectra can be utilized as a probe (called hereafter "conformational probe"). The approach is based on imbedding a small amount of the probe into the studied glass forming liquid (called hereafter "matrix") and following the temperature dependences of its conformationally sensitive bands in FTIR spectra. If at a certain condition the probe molecules can transform from one conformation (A) to another (B) within the observation time, *i.e.*, the conformers are in equilibrium, then the integrated intensities of the IR bands of the conformers, D_A and D_B, follow the relation [4]:

$$\ln\frac{D_A}{D_B} = \ln\frac{\alpha_A}{\alpha_B} + \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT}, \quad (1)$$

where ΔS_0 and ΔH_0 are the entropy and enthalpy differences of the conformers, respectively, α_A and α_B are the absorption coefficients of the conformer's bands under study, T is the temperature and R is the gas constant.

The conformational transitions in the probe molecules are possible only if the molecules of the surrounding matrix (or their fragments) exhibit sufficient mobility and if such mobility leads to creation of free volume entities large enough for the probe molecules to transform. Lowering the temperature may cause freezing-in of the molecular mobility of the matrix and this in turn may freeze-in the conformational transitions in the probe. Then below a certain temperature T_f, Eq. (1) transforms to:

$$\ln\frac{D_A}{D_B} = \ln\frac{\alpha_A}{\alpha_B} + \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT_f}, \quad (T < T_f), \quad (2)$$

where T_f is the temperature at which the conformational transitions in the probe "froze-in".

The magnitude of T_f can be determined from the curvature of the dependence of $\ln(D_A/D_B)$ upon T^{-1}. Then, knowing the "activation volume" (*i.e.*, the minimum volume required for conformational transitions to occur), one can estimate the size of the mobile units of the matrix which also froze-in at T_f.

The conformational probe must satisfy the following requirements. (i) The conformationally sensitive IR bands must be strong enough and do not overlap with the peaks of the studied matrix (*i.e.*, fall within the "transparency windows" of the matrix). (ii) The barrier hindering conformational transitions in the probe must be

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